

THERMAL ANALYSIS STUDIES OF THE CURE BEHAVIOR OF THE RESIN BINDER IN A CARBONACEOUS CEMENT

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INTRODUCTION

Artificial graphite blocks, bonded together with carbonaceous cements¹ composed of low-temperature thermosetting resins and carbonaceous fillers, have been used extensively in the aerospace industry as a mold for fabricating composite materials. Recent developments in high-performance composite materials have resulted in the use of thermosetting resins with cure and use temperatures above the decomposition temperature of conventional carbonaceous cements. A high-temperature, high-strength carbonaceous cement was developed to bond together pieces of large graphite molds used in curing these high-performance composites.² In this paper, we discuss the application of thermal analysis techniques as an aid in the development of a particular version of the high-temperature cement whose binder phase consisted of 22 wt.% fluorinated polyimide resin,³ 74 wt. % furfuryl alcohol, and 4 wt.% of a 50% ZnCl₂ solution.

EXPERIMENTAL

Differential Scanning Calorimetry (DSC) analyses were performed using either a Dupont (now TA Instruments) Pressure DSC cell or standard DSC cell mounted on a 910 cell base interfaced to a Dupont 9900 controller. DSC samples (5-25 mg) were encapsulated in standard aluminum DSC pans which had a pinhole in the upper lid to allow release of volatiles. Thermogravimetric Analyses (TGA) were performed using a Dupont 951 thermogravimetric cell base interfaced to the same controller and analysis system used for the DSC. Thermal microscopy observations were carried out using the modified Kofler hot-stage/Leitz microscope apparatus that was used previously to study mesophase pitches.⁴ Dynamic Mechanical Analyses (DMA) were carried out using a Dupont 982 DMA equipped with a 1090 controller system. Strips (8 mm wide) of a carbonized ink blotter impregnated with the liquid binder phase were mounted in the 982 DMA using the horizontal clamping assembly for the analyses.

RESULTS AND DISCUSSION

Thermogravimetry - Figure 1 shows typical TGA weight loss curves for the furfuryl alcohol/ZnCl₂ catalyst system, the polyimide resin, and the cement. The furfuryl alcohol system lost approximately 35% of its starting weight by 100°C due to loss of water. The second small weight loss between 150°C and 200°C is attributed to volatilization of the furfuryl alcohol monomer and polymerization by-products. The polyimide TGA showed a minor weight loss near 100°C due to adsorbed moisture, followed by curing until decomposition began at approximately 400°C. Weight loss due to the curing reaction of the polyimide was not apparent. The weight losses observed in the curve for the cement correspond to those of the individual resin components, indicating that the two resins react nearly independently.

Differential Scanning Calorimetry - Figure 2 shows the DSC curves for the furfuryl alcohol/ZnCl₂ catalyst and polyimide run individually. The furfuryl alcohol exothermic curing peak has an onset temperature of 107°C and a peak temperature of 131°C. The polyimide has an onset temperature of 200°C and peak temperature near 244°C. Figure 3 is the DSC curve of the cement containing both resins with exothermic peaks at 141°C and 244°C; these peaks can be assigned to the individual furfuryl alcohol and polyimide resin curing reactions, respectively. Results for the cement system showed an upward shift in the peak temperature for the curing of the furfuryl resin, but no change in the cure behavior of the polyimide resin. The change in reactivity of the furfuryl resin is attributed to the presence of the carbonaceous filler.

Thermal Microscopy -- A freshly prepared sample of the cement binder phase heated in the 135°-155°C range showed vigorous movement of gas bubbles, attributed to the evolution of by-product water from the ZnCl₂-catalyzed polymerization of furfuryl alcohol, and weight loss due to vaporization of unreacted furfuryl alcohol. The remaining binder phase was a transparent single-phase material with a pale, yellow color, which showed no physical changes when heated through the 155°-300°C range. Curing of the polyimide component of the binder at 240°C did not produce any physical change that could be detected by thermal microscopy. The remaining material charred as it was heated through the 300°-400°C range with copious gas evolution and shrinkage of the sample.

Hot-stage microscopy observations of the polyimide alone showed that it melted to a clear, fairly viscous liquid between 165°C and 210°C. Movement of the liquid ceased in the 210°-240°C range due to the resin-curing reaction. The cured polyimide resin gradually developed a red color while being heated in the 240°-325°C range, but it did not soften enough to flow freely. The resin continued to darken as it was heated up to 400°C and showed some modest shrinkage.

Dynamic Mechanical Analysis -- Figure 4 shows typical DMA data collected during the first 100 min. of a run where the complete resin binder phase was heated at 5°C/min. up to a 240°C hold temperature. The initial resonant frequency (storage modulus) at room temperature was high because some of the furfuryl alcohol solvent had evaporated during the storage period between blotter impregnation and the DMA run. The frequency decreased steadily as the binder phase softened while being heated at 5°C/min. There was a distinct peak in the damping signal (loss modulus) at ~135°C. Based on the DSC, TGA, and thermal microscopy data given above, this damping peak was attributed to: (1) the cure reaction of the furfuryl alcohol + ZnCl₂ catalyst component, and (2) vaporization of excess furfuryl alcohol solvent, leaving the solid polyimide phase behind. From the

thermal microscopy observations, the decreases in the frequency and the damping signals in the 135°-200° C range were attributed to softening of the unreacted polyimide component of the binder. Separate DMA runs with blotters impregnated with the furfuryl alcohol + ZnCl₂ catalyst mixture alone and with the polyimide dissolved in an inert solvent were consistent with these explanations for the low-temperature damping peak and the resonant frequency curve.

The second damping peak at ~ 4 min. into the hold period at 240° C in Figure 4 is attributed to vitrification of the polyimide component of the binder phase during its curing reaction. The frequency leveled off after this damping peak because the curing reaction becomes slower and diffusion-controlled after vitrification.

The DMA curve obtained when the binder-impregnated blotter from Figure 4 was reheated at 2° C/min. up to 400° C showed a distinct damping peak at 284° C and a drop in the frequency (storage modulus) which correspond with the glass transition reported by Capo and Schoenberg for this cured polyimide³. However, the frequency did not decrease down to the baseline value for the blotter alone above 300° C, so it appears that the binder phase did not soften enough to become a freely flowing liquid when it was heated to temperatures above the T_g of the polyimide component. Apparently, the fully cross-linked, polymerized furfuryl alcohol component of the binder phase provides enough residual stiffness to prevent free flow in the 280°-400° C range.

CONCLUSIONS

The thermal analyses studies showed that the two primary components of the binder phase in this cement, a fluorinated polyimide and the furfuryl alcohol + ZnCl₂ catalyst combination, cured essentially independently at distinctly different temperatures. Furfuryl alcohol has a dual role in this system, functioning initially as a solvent for the polyimide and then as a reactive monomer with the ZnCl₂ catalyst. Interestingly, this multicomponent system cures to yield an apparently single-phase material, as judged by optical microscopy observations. Thermal analysis methods proved to be very valuable in unraveling the complexities of the cure behavior of this high-temperature cement system.

ACKNOWLEDGEMENTS

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REFERENCES

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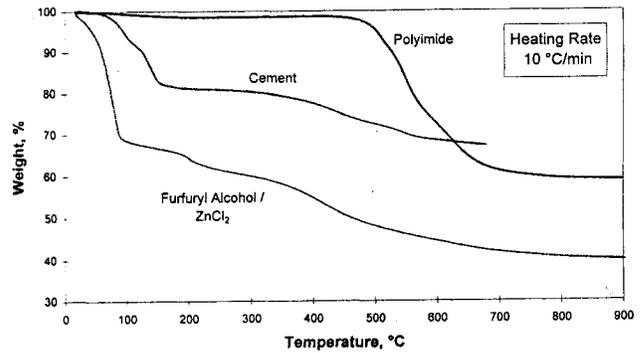


Figure 1. TGA Weight Loss Curves

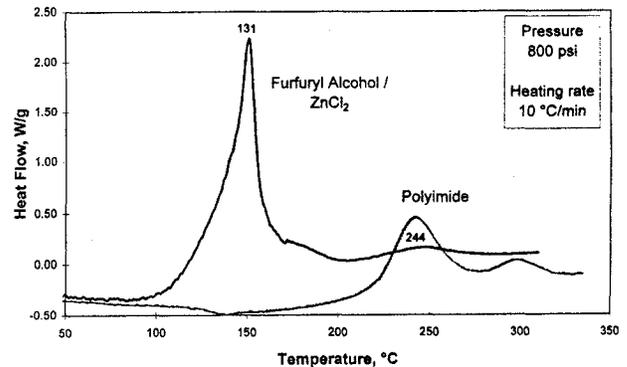


Figure 2. Pressure DSC Curves for Binder Components

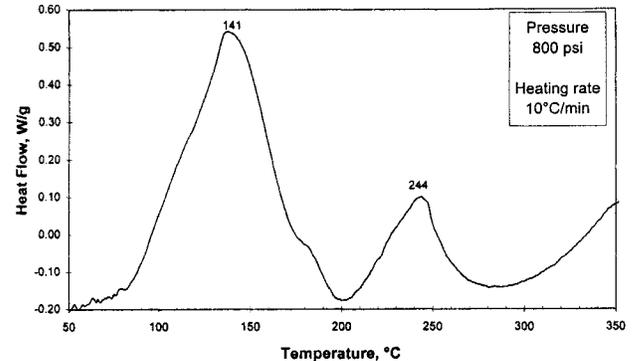


Figure 3. Pressure DSC Curve for Cement

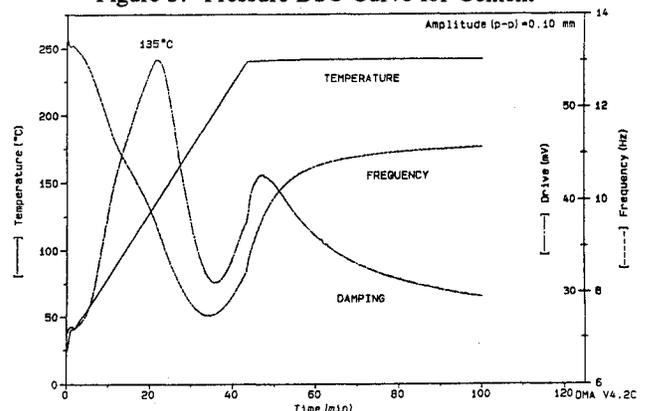


Figure 4. DMA Curve for Binder System Cure at 240° C